Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 75 (2007) 770–775
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Short communication

Synthesis, structure and electrochemical properties of 2,5-bis(alkyl/arylamino)1,4-benzoquinones and 2-arylamino-1,4-naphthoquinones

Syamaprasad Bayen, Nilotpal Barooah, Rupam J. Sarma, Tamal Kumar Sen,
A. Karmakar, Jubaraj B. Baruah*

Department of Chemistry, Indian Institute of Technology, Guwahati 781 039, India

Received 12 July 2006; received in revised form 21 July 2006; accepted 27 July 2006
Available online 6 October 2006

Abstract

Various primary amines react with 1,4-benzoquinone to form corresponding 2,5-bis(alkyl/arylamino)1,4-benzoquinone. The crystal structure of three such derivatives namely 2,5-bis(2-propylamino)1,4-benzoquinone, 2,5-bis(cyclohexylamino) 1,4-benzoquinone and 2,5-bis(3-methylanilino)1,4-benzoquinone is determined. The solid-state structure shows absence of intra-molecular hydrogen bonding between the carbonyl of the quinone unit with N−H of the amine group in these molecules. Each of these compounds shows a proton sensitive quasi-reversible redox couple. Analysis on the basis of torsion angle shows that conjugation of the O═C−C−N frame has lesser contribution to the quasi-reversible cycle but the couple is effected by variation of the substituents on the nitrogen atom. The reaction of 1,4-naphthoquinone with primary amines also gives corresponding 2-amino-1,4-naphthoquinone derivatives. Two representative crystal structures of 2-amino-1,4-naphthoquinone derivatives are reported.

Keywords: Aminoquinone; Selective synthesis; Crystal structure; H-bonding; Cyclic voltamogram

1. Introduction

Quinonic compounds are of great importance to understand different processes that are related to biology [1]. They have application in synthetic organic chemistry [2]. From the perspectives of designing magnetic materials [3] and understanding photo-physical properties [4], the co-ordination chemistry of quinones is also very important. Metal-quinonoid complexes also show valence tautomerism [5]. Substantial amount of research is done on the quinonic polymers to use them as photo-conductors [6]. The quinones also find application as electrode material [7]. The redox properties of quinones are useful in designing multiple cycled metal catalysed oxidation processes [8]. Palladium quinone complexes are of great importance in synthetic organic chemistry as catalyst [9]. The amino-quinones are used as herbicides [1d], but their redox properties are less studied. With this background we set our study to synthesise and characterise a series of nitrogen containing quinonic compounds having the framework as shown in Fig. 1. Although it is already reported that the reaction of 1,4-benzoquinone with organic amine gives amino-quinones [10], these reactions are not explored systematically for

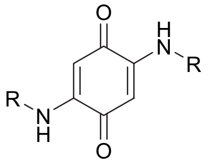


Fig. 1.

---

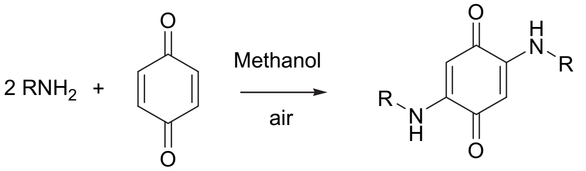
* Corresponding author.
E-mail address: juba@iitg.ernet.in (J.B. Baruah).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.07.033

selective synthesis of bis-amino-quinones. Moreover, selective synthesis of amino-quinones would provide guideline for synthesis of interesting quinone based compounds for material design. The structural aspect of such compounds is not yet studied and understanding of structural feature will help in synthesis of novel metal complexes similar to the one reported in the literature [5]. In this article, we show an exceptionally simple yet selective one pot synthesis of 2,5-bis(alkyl/arylamino)1,4-benzoquinones and their structure and electrochemical properties.

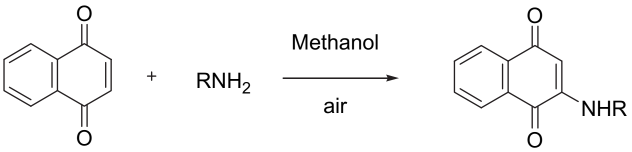
2. Result and discussions

A series of 2,5-bis(alkyl/arylamino)1,4-quinones are synthesised from the reaction of 1,4-benzoquinone with different amines under aerobic condition as illustrated in Eq. (1).



R = -CH(CH$_3$)$_2$ (**1**); -(CH$_2$)$_3$CH$_3$ (**2**); -cyclo-C$_6$H$_{11}$ (**3**); o-CH$_3$C$_6$H$_4$- (**4**); 3-CH$_3$C$_6$H$_4$- (**5**); o-CH$_3$OC$_6$H$_4$- (**6**); C$_6$H$_5$CH$_2$- (**7**); -CH$_2$CH$_2$OH (**8**); -CH$_2$CH$_3$ (**9**) (1)

The reaction is found to be exceptionally selective and leads to only 2,5-bis(alkyl/arylamino)1,4-benzoquinones of the corresponding amine. From the reaction mixture the products can be simply filtered and recrystallised. The results on these reactions are listed in Table 1. From these reactions we could not obtain 2,6-bis(alkyl/arylamino)1,4-benzoquinone derivatives. The minimum energy (calculated by MM2 using Chem3D pro version 7.00) of 2,5-bis(amino)1,4-benzoquinone and 2,6-bis(amino)1,4-benzoquinone are very comparable but with a difference of 0.04 kcal. This suggests that the steric factors arising from the substituent effect predominates in these reactions. The result of selective formation of 2,5 isomer may be assumed to be due to attack of two amines to 1,4-benzoquinone. For such attack to give exclusive product of one isomer would require approach of two amines from the furthest possible distance. Thus, exclusively 2,5 isomer is formed due to electrostatic reasons. This is also evident from the fact that 1,4-naphthoquinone on reaction with amines gives monosubstituted derivatives. We have also carried out reaction with ammonia with 1,4-benzoquinone, however; in this case, the products could not be obtained in pure and soluble form. However, the reactions of primary amines with 1,4-benzoquinone lead to precipitation of the product making it difficult to follow the kinetics of the reaction by NMR experiment. It is interesting to note that the reactions of aniline having electron-donating substrates react well with 1,4-benzoquinone but with electron deficient systems such as 4-nitro-aniline the reaction did not work at room temperature. On heating the reaction mixture it led to mixture of products, which could not be purified. In this regard, it may be mentioned that the 2-aminobenzoic acid has been reported to react with 1,4-benzoquinone [10g], thus, the nature of substituent plays a role in these reactions. For example, 1,4-naphthoquinone reacts with different amines to give corresponding mono-substituted 2-amino-1,4-naphthoquinones (Eq. (2)).

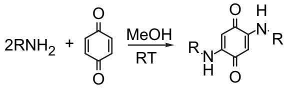


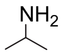
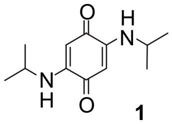
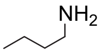
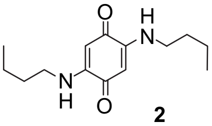
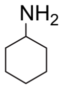
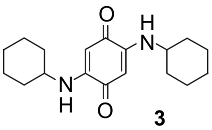
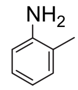
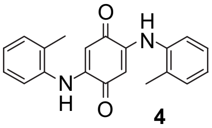
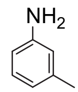
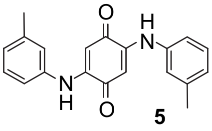
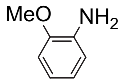
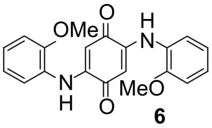
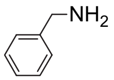
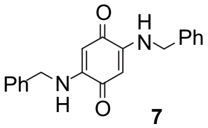
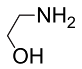
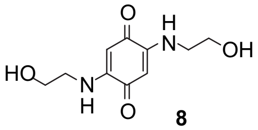
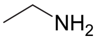
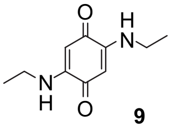
When R = *p*-CH$_3$OC$_6$H$_4$ (**10**), (o-CH$_3$O)(p-CH$_3$O)C$_6$H$_3$- (**11**) (2)

Hydrogen bonding has an important role in deciding properties of quinonic compounds [11]. With anticipation that these molecules will have intra-molecular hydrogen bonding between the N–H and the carbonyl group of the quinonic part, we have studied the crystal structure of few derivatives. Single crystal X-ray diffraction studies of a few 2,5-bis(alkyl/arylamino)1,4-benzoquinone derivatives show that they exist as dimers in solid state through N–H···O hydrogen bonding interactions. An illustrative example showing such a dimeric form in the crystal structure of **1** is given in Fig. 2. The asymmetric unit of this compound contains two molecules. It is observed that the molecules self-assemble in the solid state through intermolecular N–H···O ($d_{O1\cdots N1}$ 3.019 Å, 161.2°) hydrogen bonds. In this compound, there is no intra-molecular hydrogen bonding among the carbonyl of the quinone ring and N–H of the amino groups. Similarly, the crystal structures of **3** and **5** are determined (Fig. 3) and in these cases also we did not observe the intra-molecular hydrogen bonding between the carbonyl and NH groups.

Compounds **1**–**9** are derived from 1,4-benzoquinone, thus they are expected to show electrochemical properties similar to that of 1,4-benzoquinone [12]. Cyclic voltamogram of these compounds is recorded in acetonitrile as solvent with tetrabutyl ammonium perchlorate as supporting electrolyte. From the ΔE_p and i_p/i_c values it is found that each of these compounds has a quasi-reversible redox couple in the negative voltage side. The $E_{1/2}$ values for the couples and the i_p/i_c values are listed in Table 2. Since delocalisation plays a crucial role in redox processes and these molecules have a carbonyl group next to an amine group, the effect of delocalisation is expected to play a crucial role in deciding their electrochemical properties. Delocalisation involving the carbonyl of quinonic ring would depend on the planarity of the ring with the amine group, this should cause the differences in observed redox properties and deviation from the redox properties of the parent 1,4-benzoquinone. Thus, from the crystal structure of the three compounds **1**, **3** and **5**, we have analysed the torsion angle about O=C–C–N bonds. The torsion angles around O=C–C–N are found to

Table 1
Reactions of 1,4-benzoquinone with various amines



Amines	Time (h)	Product	Isolated yield (%)
	15	 **1**	88
	14	 **2**	70
	15	 **3**	80
	15	 **4**	80
	15	 **5**	81
	15	 **6**	73
	16	 **7**	72
	13	 **8**	85
	14	 **9**	85

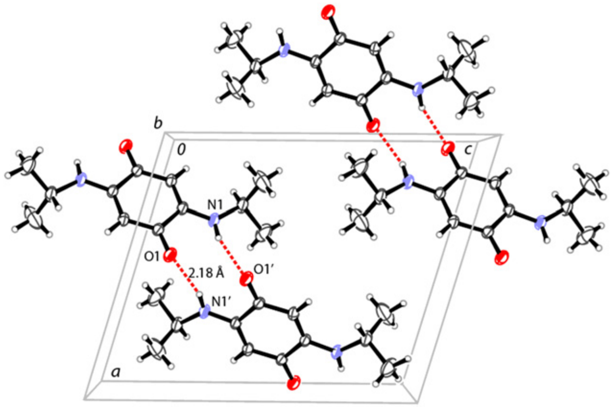
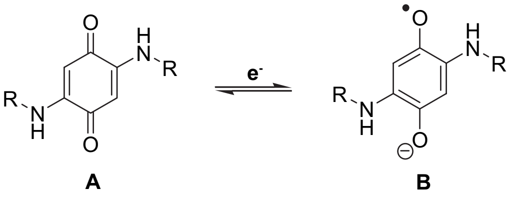


Fig. 2. Crystal structure of 2,5-bis(2-propylamino)1,4-benzoquinone, **1** (thermal ellipsoids drawn to 30% probability); hydrogen bonding interactions between the N–H and the C=O groups lead to a layered structure parallel to *ac*-plane.

be 0.98°, −2.39°, −3.68° for **1**, **3** and **5**, respectively. From this it is clear that the planarity of the O=C–C–N frame in these molecules is in the order of **1** > **3** > **5**. However, the deviation from reversibility in the redox couple is in the order of **3** > **1** > **5**. So, the deviation from reversibility in the observed redox couple is not purely an electronic factor related to the twist arising out of the bond angle along O=C–C–N bond deciding the orientation of the amine and carbonyl groups but may be related to the electronic effect of the substituents.

In a similar manner naphthoquinone derivatives are also characterised by their X-ray crystal structure. Two representative structures of compounds **10** and **11** are shown in Fig. 4. Analogous to the aminoquinone structure discussed earlier these compounds also do not have intra-molecular hydrogen bonding among the NH group and the adjacent carbonyl group. But in the lattice they self-assemble through the intermolecular hydrogen bonding among NH and the carbonyl oxygen atoms.

The 1,4-benzoquinone itself shows two reversible redox couples in the negative potentials [12] corresponding to two one-electron redox couples due to stepwise formation of mono- and bi-anion radical. But in the compounds reported here we observe only one electrochemical redox couple, which is attributed to the electrochemical process as illustrated in Eq. (3). Unlike 1,4-benzoquinone, the second electron transfer process in these compounds (**1**–**8**) is difficult and it is obvious that a di-anion would not be favored in an aromatic ring system having two electron-donating amine functionality. It is supported by the fact that the di-anion of 1,4-benzoquinones is also proton sensitive [12] and the labile protons in these systems affect the second redox process. In our compounds, there is already a source for labile protons, which disfavors di-anion formation.



(3)

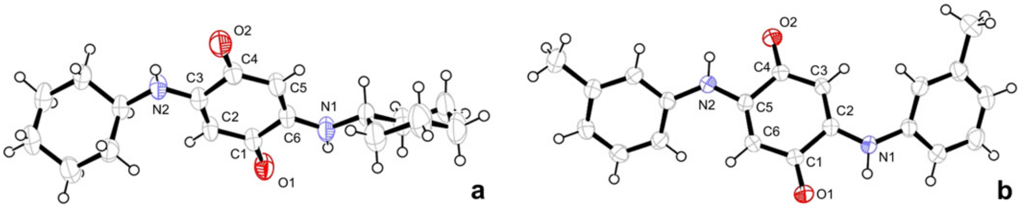


Fig. 3. Crystal structure (a) 2,5-bis(cyclohexylamino)1,4-benzoquinone (**3**) and (b) 2,5-bis(3-methylanilino)1,4-benzoquinone (**5**) drawn with 30% thermal ellipsoid.

It is also found that the redox couples observed for these molecules are acid sensitive. For example, addition of acetic acid to solutions of these quinonic compounds causes new reduction peaks to appear at a lower value. Further to this, on addition of acetic acid the redox couple of the parent compound becomes irreversible and the reduction process becomes prominent but the oxidation process is inhibited. The changes brought about by the addition of acid in the electrochemical process for compound **2** are illustrated in Fig. 5. The new reduction peak, which appeared on addition of acid to a solution of **2** is attributed to the formation of a fraction of protonated 2,5-bis(*n*-butylamino)1,4-benzoquinone on addition of acetic acid and its reduction. These observations show that the redox process in these compounds is controlled by hydrogen ion concentration. Since these compounds have nitrogen atoms, which can be easily protonated, this inhibits the reversibility of the redox process. In terms of electrochemistry, compounds **10** and **11** are analogous to the aminobenzoquinones discussed earlier. These compounds possess a reversible couple in the range of −790 to −800 mV due to the formation of radical anion.

In conclusion, we have prepared a series of 2,5-bis(alkyl/arylamino)1,4-benzoquinones through a selective one step procedure. The crystal structure of three such derivatives **1**, **3** and **5** showed absence of intra-molecular hydrogen bonding among the carbonyl and amine group in them. The 2,5-bis(alkyl/arylamino)1,4-benzoquinones show a proton sensitive quasi-reversible redox couple.

2.1. Experimental section

The ^1H NMR spectra were recorded in a Varian 400 MHz spectrophotometer at room temperature; while the FT-IR spectra were recorded in NICOLET IMPACT-410 spectrometer using OMNIC software. Electrochemical studies were performed in acetonitrile (10 ml) solution containing approximately 2–4 mg (∼0.1 mmol) of each compound along with tetrabutyl ammonium perchlorate (200 mg) as supporting electrolyte. The cyclic voltamograms were recorded under nitrogen atmosphere with three electrode system comprising platinum as working and auxiliary electrodes with an Ag/AgCl reference electrode in a CHI660A electrochemical workstation. The scan speed used was 100 mV s^{-1}. All the melting points reported are uncorrected. The X-ray diffraction data were collected on Bruker 3-circle SMART Apex diffractometer with CCD area detector, using graphite monochromated Mo Kα radiation from a 60 W microfocus Bede Microsource® with glass polycapillary optics. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software [13].

Table 2
The electrochemical parameters for compounds **1–8**

Compound	$E_{1/2}$ (V)	i_p/i_c	ΔE_p (V)
1	−1.0415	1.10	0.167
2	−1.051	1.00	0.136
3	−0.687	1.95	0.294
4	−0.616	1.34	0.377
5	−0.777	1.38	0.101
6	−0.756	1.72	0.075
7	−0.763	1.11	0.105
8	−0.965	1.09	0.091

2.2. General procedure for synthesis of 2,5-bis(alkyl/arylamino)1,4-benzoquinones (*1–9*)

In a typical experiment, 2-propylamine (600 mg, 10.2 mmol) was added dropwise to a well-stirred solution of 1,4-benzoquinone (540 mg, 5 mmol) in methanol (15 ml) at room temperature. On addition of amine, the yellow color due to the parent quinone disappeared and the solution turned black. The solution was stirred for 15 h, after which the volume of the solution was made to half under reduced pressure. A brown precipitate appeared, the precipitate was filtered and dried at room temperature and further recrystallised from MeOH to obtain 2,5-bis(2-propylamino)1,4-benzoquinone. Other 2,5-bis(alkyl/arylamino)1,4-benzoquinones were prepared in analogous manner from their corresponding amines.

2.3. Analytical data for compounds *1–9*

2.3.1. 2,5-Bis(2-propylamino)1,4-benzoquinone (*1*)

Melting point: 185 °C. Elemental anal. calcd. for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60; found C, 64.43; H, 8.12; N, 12.52. ^1H NMR ($CDCl_3$, 400 MHz, ppm): 1.32 (d, $J = 6.8$ Hz, 12H), 3.65 (heptet, $J = 6.8$ Hz, 2H), 6.50 (br s, 2H), 6.70 (s, 2H). IR (KBr, cm^{-1}): 3210 (s), 2976 (s), 1564 (s), 1487 (s), 1314 (s), 1228 (s), 1131 (s), 835 (m), 723 (m). UV–vis (χ_{max}, CH_3CN) 341 nm ($\varepsilon = 15{,}387.6$ cm^{-1} M^{-1}); crystal data and refinement parameters for compound **1** are: Crystal system, Monoclinic; Space group C2/c, $a = 10.7806(8)$ Å; $b = 9.1044(8)$ Å, $c = 12.8759(10)$ Å, $\beta = 106.501°$, $V = 1211.73(17)$ Å^3, $Z = 4$; Density (Mg m^{-3}), 1.218; Abs. Coeff.

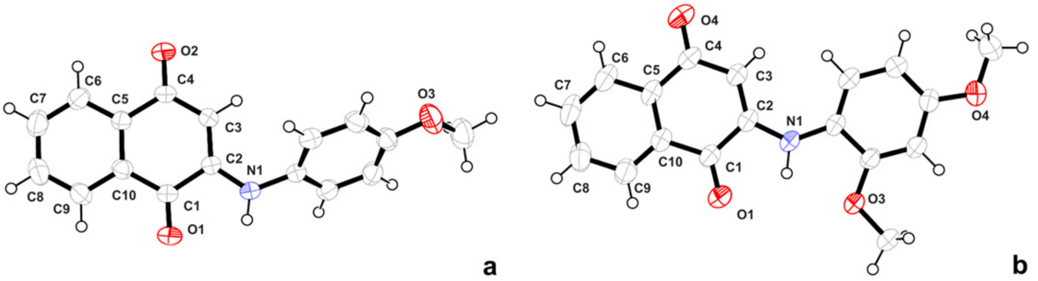


Fig. 4. The crystal structure of (a) 2-(4-methoxyanilino)1,4-naphthoquinone (**10**) and (b) 2-(2,4-dimethoxy anilino)1,4-naphthoquinone (**11**) drawn with 30% thermal ellipsoid.

(mm^{-1}), 0.084; Total number of reflections, 26,763; Refinement method, full-matrix least-squares on F^2; Data/Restraints/Parameters, 1428/0/83; Goof (F^2), 1.031; R indices $[I > 2\sigma(I)]$, 0.0458; R indices (all data), 0.0704.

2.3.2. 2,5-Bis(n-butylamino)1,4-benzoquinone (2)

Melting point: 154 °C. Elemental anal. calcd. for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; found C, 67.34; H, 8.81. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 0.95 (t, 6H, $J = 7.4$ Hz), 1.41 (septate, 4H, $J = 7.4$ Hz), 1.63 (m, 4H), 3.14 (q, 4H, $J = 7.4$ Hz), 5.29 (s, 2H), 6.58 (br s, 2H). IR (KBr, cm^{-1}): 3261 (s), 2956 (s), 2862 (m), 1643 (s), 1551 (s), 1499 (s), 1458 (w), 1363 (s), 1293 (s), 1250 (s), 1207 (w), 1078 (w), 910 (w), 674 (br s).

2.3.3. 2,5-Bis(cyclohexylamino)1,4-benzoquinone (3)

Melting point: 236 °C. Elemental anal. calcd. for $C_{18}H_{26}N_2O_2$: C, 71.49; H, 8.67; found C, 71.65; H, 8.62. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 1.31 (m, 12H), 1.77 (m, 4H), 1.97 (m, 4H), 3.25 (m, 2H), 5.31 (s, 2H), 6.58 (s, 2H). IR (KBr, cm^{-1}): 3268 (s), 2925 (s), 2853 (s), 1644 (s), 1593 (w), 1568 (s), 1496 (s), 1358 (s), 1301 (s), 1255 (s), 1214 (s). Unit cell parameters: Monoclinic, space group P21/c, $a = 14.2272(10)$ Å, $b = 8.9925(7)$ Å, $c = 13.3769(9)$ Å, $\beta = 99.370(5)°$, $Z = 4$, Density (Mg m^{-3}), 1.190; Abs. Coeff. (mm^{-1}), 0.078; Total number of reflections, 12,276; Refinement method, full-matrix least-squares on F^2; Data/Restraints/Parameters, 4477/0/295; Goof (F^2), 1.033; R indices $[I > 2\sigma(I)]$, 0.0499; R indices (all data), 0.0997.

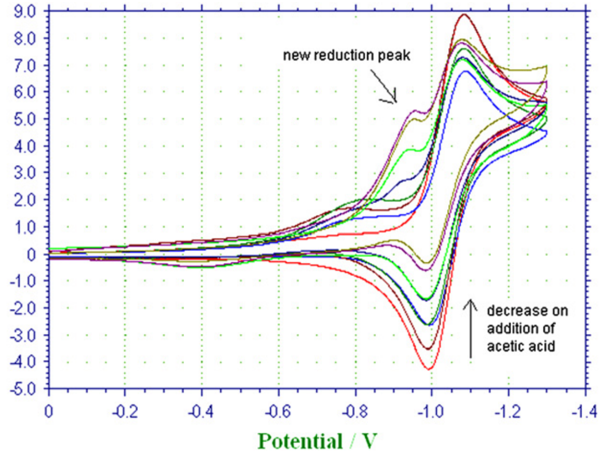


Fig. 5. Cyclic voltamogram of **2** (1 mmol) in acetonitrile (10 ml) on addition of acetic acid (10 mM) solution in aliquots of 10 µl.

2.3.4. 2,5-Bis(2-methylanilino)1,4-benzoquinone (4)

Melting point: 253–254 °C. Elemental anal. calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; found C, 75.35; H, 5.68. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 2.28 (s, 6H), 5.65 (s, 2H), 6.19 (m, 2H), 7.03 (m, 2H), 7.28–7.19 (m, 4H), 7.87 (br s, 2H). IR (KBr, cm^{-1}): 3241 (s), 2928 (w), 2361 (b), 1644 (s), 1570 (s), 1504 (s), 1492 (w), 1353 (s), 1289 (s), 1163 (s), 1100 (m), 853 (w), 782 (s), 743 (w).

2.3.5. 2,5-Bis(3-methylanilino)1,4-benzoquinone (5)

Melting point: 257–259 °C. Elemental anal. calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; found C, 74.98; H, 5.65. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 2.38 (s, 6H), 6.06 (s, 2H), 7.04 (m, 4H), 7.27 (m, 4H), 8.06 (s, 2H). IR (KBr, cm^{-1}): 3738 (b), 3241 (s), 2928 (w), 2361 (b), 1640 (s), 1570 (s), 1504 (s), 1492 (w), 1353 (s), 1289 (s), 1199 (s), 1163 (m), 853 (w), 782 (s), 743 (w), 723 (w). Unit cell parameters for crystal: Monoclinic, space group P21/n, $a = 14.1207(7)$ Å, $b = 7.2327(4)$ Å, $c = 15.5611(8)$ Å, $\beta = 92.965(2)°$, $Z = 4$; Density (Mg m^{-3}), 1.332; Abs. Coeff. (mm^{-1}), 0.087; Total number of reflections, 13,547; Refinement method, full-matrix least-squares on F^2; Data/Restraints/Parameters, 4135/0/227; Goof (F^2), 0.992; R indices $[I > 2\sigma(I)]$, 0.0533; R indices (all data), 0.0983.

2.3.6. 2,5-Bis(2-methoxyanilino)1,4-benzoquinone (6)

Melting point: 250 °C. Elemental anal. calcd. for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; found C, 68.76; H, 5.21. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 3.98 (s, 6H), 6.15 (s, 2H), 6.93 (d, 2H), 6.98 (m, 4H), 7.13 (t, 2H, $J = 7.4$ Hz), 7.40 (d, 2H, $J = 7.4$ Hz), 8.45 (s, 2H). IR (KBr, cm^{-1}): 3298 (s), 3236 (w), 1655 (s), 1583 (s), 1527 (s), 1481 (s), 1460 (s), 1352 (s), 1286 (s), 1250 (s), 1189 (s), 1122 (s), 1025 (s), 728 (w).

2.3.7. 2,5-Bis(benzylamino)1,4-benzoquinone (7)

Melting point: 234 °C. Elemental anal. calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; found C, 75.13; H, 5.68. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 4.32 (d, 4H, $J = 6$ Hz), 5.37 (s, 2H), 6.75 (br s, 2H), 7.36–7.24 (m, 10H). IR (KBr, cm^{-1}): 3279 (s), 3021 (s), 1643 (s), 1496 (s), 1362 (s), 1253 (s), 1059 (w), 1004 (m), 856 (w), 814 (br s), 697 (br s).

*2.3.8. 2,5-Bis(ethanolamino)1,4-benzoquinone (**8**)*

Melting point: >350 °C. Elemental anal. calcd. for $C_{410}H_{14}N_2O_4$: C, 53.09; H, 6.24; found C, 53.18; H, 6.45. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 3.18 (t, 4H, $J = 4.6$ Hz), 3.58 (q, 4H, $J = 6.4$ Hz), 4.87 (br s, 2H), 7.37 (br s, 2H), 8.20 (s, 2H). IR (KBr, cm^{-1}): 3317 (br s), 3254 (w), 3215 (s), 3150 (s), 1628 (s), 1550 (s), 1491 (br s), 1446 (m), 1381 (w), 1301 (s), 1262 (s), 1073 (s), 710 (s).

*2.3.9. 2,5-Bis(ethylamino)1,4-benzoquinone (**9**)*

Melting point: 218 °C. Elemental anal. calcd. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; found C, 61.68; H, 7.23. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 1.29 (t, 6H, $J = 7.6$ Hz), 3.19 (m, 4H), 5.23 (s, 2H), 6.51 (s, 2H). IR (KBr, cm^{-1}): 3281 (s), 2972 (s), 2932 (w), 2868 (w), 1644 (w), 1550 (br s), 1486 (br s), 1367 (s), 1267 (s), 1227 (m), 1134 (m), 1096 (m), 1057 (s), 906 (w), 812 (m), 792 (s), 768 (w), 708 (br s), 467 (m).

The 1,4-naphthoquinone derivatives are prepared by stirring a homogeneous methanolic solution of 1,4-naphthoquinone and corresponding amine at room temperature. Brown to dark red precipitate was obtained in cases. Recrystallisation of these precipitates from methanol gave the corresponding compounds in pure form.

*2.3.10. 2-(4-Methoxyanilino)1,4-naphthoquinone (**10**)*

Melting point: 162–170 °C. Yield: 85%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 3.82 (s, 3H), 6.20 (s, 1H), 6.94 (d, $J = 8$ Hz, 2H), 7.19 (d, $J = 8$ Hz, 2H), 7.40 (br s, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 8.1 (t, $J = 5.6$ Hz, 2H). IR (KBr, cm^{-1}): 3428 (br s), 3223 (s), 1676 (s), 1566 (s), 1601 (s), 1508 (s), 1355 (s), 1289 (s), 1234 (s), 1122 (s), 1039 (s), 721 (s). Unit cell parameters for crystal: Monoclinic, space group P21/n, $a = 3.99740(10)$ Å, $b = 27.8247(9)$ (4) Å, $c = 11.9691(4)$ Å, $\beta = 96.658(2)°$, $Z = 4$; Density (Mg m^{-3}), 1.403; Abs. Coeff. (mm^{-1}), 0.097; Total number of reflections, 10,862; Refinement method, full-matrix least-squares on F^2; Goof (F^2), 0.978; R indices [$I > 2\sigma(I)$], 0.0470; R indices (all data), 0.0834.

*2.3.11. 2-(2,4-Dimethoxy anilino)1,4-naphthoquinone (**11**)*

Melting point: 150–153 °C, Yield: 77%. ^{1}H NMR (CDCl, 400 MHz, ppm): 3.82 (s, 3H), 3.86 (s, 3H), 6.27 (s, 1H), 6.48–6.53 (m, 2H), 7.28 (d, $J = 8$ Hz, 1H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.68 (br s, 1H), 7.72 (t, $J = 7.2$ Hz, 1H), 8.08 (t, $J = 6.4$ Hz, 2H). IR (KBr, cm^{-1}): 3339 (br s), 3310 (s), 2940 (w), 1672 (s), 1621 (s), 1542 (s), 1363 (s), 1329 (s), 1293 (s), 1269 (s), 1208 (s), 1139 (s), 1026 (s), 726 (s). Unit cell parameters for crystal: Monoclinic, space group P-1, $a = 7.3277(3)$ Å, $b = 9.1243(4)$ Å, $c = 11.7908(4)$ Å, $\alpha = 84.626(3)$, $\beta = 81.823(3)$, $\gamma = 68.745(3)°$, $Z = 2$; Density (Mg m^{-3}), 1.414; Abs. Coeff. (mm^{-1}), 0.101; Total number of reflections, 7832; Refinement method, full-matrix least-squares on F^2; Goof (F^2), 0.922; R indices [$I > 2\sigma(I)$], 0.0444; R indices (all data), 0.0853.

Acknowledgement

The authors thank Council of Scientific and Industrial Research, New Delhi, India for financial assistance and Department of Science and Technology, New Delhi for X-ray facility.

Appendix. Supplementary materials

The crystallographic information of **1**, **3**, **5**, **10** and **11** is deposited to Cambridge Crystallographic Database and has the CCDC numbers 607637 for **1**, 610155 for **3**, 610156 for **5**, 612934 for **10**, and 612935 for **11**.

References

[1] (a) Xu M, Lukeman M, Wan P. Photochem Photobiol 2006;82:50–6;
(b) Cramer WA, Zhang H, Yan J, Kurisu G. Biochem Soc Trans 2005;33:921–3;
(c) Hartmut M, Johann D. Biochemistry 1988;27:1–7;
(d) Rutherford WA, Anja K-L. Trends Biochem Sci 2001;26:648–53;
(e) Krieger A, Weis E. Photosynthetica 1992;27:89–98;
(f) Rutherford AW, Faller P. Philos Trans R Soc Lond Ser B 2003;358:245–53.

[2] (a) Grecian S, Wrobleski AD, Aube J. Org Lett 2005;7:3167–70;
(b) Bakola-Christianopoulou MN. Appl Organomet Chem 2001;15:889–900;
(c) Yamashita H, Reddy NP, Tanaka M. Organometallics 1997;16:5223–4.

[3] Hasegawa T, Mochida T, Kondo R, Kagoshima K, Iwasa Y, Akutagawa T, et al. Phys Rev B 2000;62:10059–66.

[4] Siemiarczuk A, McIntosh AR, Ho T-F, Stillman MJ, Roach KJ, Weedon AC, et al. J Am Chem Soc 1983;105:7224–30.

[5] (a) Dei A, Gattesci D, Sangregorio C, Sorace L. Acc Chem Res 2004;37:827–35;
(b) Gutlich P, Dei A. Angew Chem Int Ed Engl 1997;36:2734–7;
(c) Pierpont CG, Lange CW. Prog Inorg Chem 1993;41:331–42;
(d) Buchanan RM, Pierpont CG. J Am Chem Soc 1980;102:4951–7;
(e) Adams DM, Dei A, Rheingold AL, Hendrickson DN. J Am Chem Soc 1993;115:8221–9;
(f) Jung O-S, Jo DH, Lee Y-A, Conklin BJ, Pierpont CG. Inorg Chem 1997;36:19–24;
(g) Wada T, Tsuge K, Tanaka K. Inorg Chem 2001;40:329–37.

[6] Ishikita H, Knapp E-W. J Am Chem Soc 2005;127:14714–20.

[7] Soriaga MP, Hubbard AT. J Am Chem Soc 1982;104:2737–45.

[8] Samec JSM, Backvall J-E, Andersson PG, Brandt P. Chem Soc Rev 2006;35:237–48.

[9] Viciu MS, Germaneau RF, Navarro-Fernandez O, Stevens ED, Nolan SP. Organometallics 2002;21:5470–2.

[10] (a) Mason HS. Nature 1955;175:771–2;
(b) Markova AN, Gribkova MP, Martynov VS, Berlin AY. Puti sinteza i Izyskaniya protivoopukholevykh Preparatov 1962;1960:165–74;
(c) Roushdi MI, Mikhail AA, Ahmed CI. Acta Pharm 1976;26:287;
(d) Martynoff M, Tsatas G, Sorbonne P. Bull Soc Chem Fr 1947;52–7;
(e) Fischer E, Schrader H. Ber Dtsch Chem Ges 1910;43:525;
(f) Cranwell PA, Haworth RD. Tetrahedron 1971;27:1831–7;
(g) Acheson RM, Sansom BF. J Chem Soc 1955;4440–3.

[11] (a) Aguilar-Martinez M, Macias-Ruvalcaba NA, Bautista-Martinez JA, Gomez M, Gonzalez FJ, Gonzalez I. Curr Org Chem 2004;8:1721–38;
(b) Okamoto K, Fukuzumi S. J Phys Chem B 2005;109:7713–23;
(c) Fukuzumi S, Okamoto K, Yoshida Y, Imahori H, Araki Y, Ito O. J Am Chem Soc 2003;125:1007–13;
(d) Tanaka K, Yamamoto Y, Machida I, Iwata S. J Chem Soc Perkin Trans 2 1999;285–8.

[12] Uno B, Kawabata A, Kano K. Chem Lett 1992;1017–20.

[13] Sheldrick GM. SHELXS97, program for the solution of crystal structures. Germany: University of Gottingen; 1997.